Effect of Chloride Concentration and pH on Pitting Corrosion of Waste Package Container Materials

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Abstract

The results of recent electrochemical study[1] performed on numerous candidate waste package container materials at the Lawrence Livermore National Laboratory indicate that iron-nickel-chromium-molybdenum (Fe-Ni-Cr-Mo) Alloys 825 and G-3 may undergo pitting corrosion in acidic brine at 90°C under potentiodynamic and potentiostatic controls. Since Alloy G-3 suffered from pitting despite its higher Mo content than Alloy 825, another Fe-Ni-Cr-Mo alloy, namely Alloy G-30, that contains more Cr than Alloy G-3, and more Mo than Alloy 825, was later included in the testing program. The results[1] indicate that Alloy G-30 may not be susceptible to pitting corrosion under a similar environmental condition.

Since the precise repository environment surrounding the waste packages is yet to be determined, previous tests[1] were performed in deaerated neutral, acidic, and alkaline solutions containing 5 weight percent (wt%) NaCl at ambient temperature, 60°C, and 90°C. The pH of these solutions ranged between 6 and 7, 2 and 3, and 10 and 11, respectively. Concentrated brines were selected to simulate a dry-out condition followed by resaturation, causing concentration of salts. It is well known[2-4] that chloride concentration and pH can have significant effects on pitting susceptibility of various metals and alloys. More recently, additional tests were performed in deaerated neutral, acidic, and alkaline brines containing 1, 5, and 10 wt% of NaCl at 90°C using cyclic potentiodynamic polarization (CPP) technique, the results of which are presented in this paper.

Materials tested include Fe-Ni-Cr-Mo Alloys 825, G-3 and G-30, Ni-base Alloys C-4 and C-22, and titanium-base Ti Gr-12. CPP tests were conducted in a Pyrex corrosion cell using a cylindrical test specimen as working electrode, two graphite counter electrodes, and a Luggin capillary connected to a reference electrode. Ag/AgCl was used as the reference electrode in all tests. The test specimens were polished with 600-grit paper and cleaned with distilled water, acetone, and ethanol prior to their exposure to the test solutions. Potential was applied to the test specimens at the ASTM-specified[5] rate of 0.17 mV/sec using EG&G Models 273 and 283 potentiostats, controlled by an IBM-compatible PC with EG&G Model 252/352 Softcorr II software. A controlled-temperature water bath contained the test cell to maintain the temperature at the desired value. The tested specimens were cleaned, followed by visual and microscopic evaluations to determine the presence or absence of pitting.

During CPP experiments, initially the test specimen is allowed to reach its stable corrosion potential (E_{corr}), followed by a forward anodic scan up to a pre-set vertex potential. A clockwise hysteresis loop is traced during reverse scan indicating the possibility of pitting in susceptible alloys. Two pitting parameters, namely the pitting potential (E_{pit}), and the protection potential (E_{prot}) can be determined from these tests. The value of E_{pit} denotes the potential at which pits initiate on the forward scan and the current increases abruptly. E_{prot} indicates the potential at which pits are repassivated during the reverse scan and the current goes back to passive values.

Figure 1 shows the plot of E_{pit} as a function of chloride concentration for Alloys 825, G-3 and G-30 in acidic brines, showing a shift in E_{pit} to more negative (or active) value with increasing chloride concentration. It is interesting to note that Alloy G-30, which did not exhibit pitting tendency in acidic solution containing 5 wt% NaCl at 90°C in earlier tests[1], did suffer from pitting corrosion at all three chloride concentration levels tested. It should, however, be mentioned that, compared to the previous ones, the vertex potential used in the present study was set at higher values. The extent of pitting in Alloy G-30 was significantly less compared to those in Alloys 825 and G-3. Alloys C-4 and C-22, and Ti Gr-12 did not exhibit any pitting susceptibility under these experimental conditions.

The relationship between E_{pit} and pH for susceptible alloys in solutions containing 10 wt% NaCl is shown in Figure 2. It is clear that for all three materials, E_{pit} was significantly shifted to more noble direction with a change in pH from acidic to neutral, as expected. At alkaline pH, Alloys G-3 and G-30 showed slightly negative E_{pit} values compared to those in neutral solution, also as expected. However, E_{pit} for Alloy 825 was shifted to a more positive value at alkaline pH.

The effect of chloride concentration on E_{pit} is consistent with that observed by other investigators[6]. In the presence of chloride, pitting of susceptible metals and alloys is due to the breakdown of protective oxide films. It has been suggested[6,7] that transition from passivity to pitting conditions can be explained by a competitive adsorption mechanism by which chloride ions (Cl⁻) move into the double layer (oxide/liquid interface), eventually reaching a critical potential, E_{pit}, corresponding to the Cl⁻ required to displace the adsorbed oxygen species. As to the pH effect, the more active E_{pit} value in acidic solution is the result of acceleration of the cathodic reaction due to the high concentration of H⁺ ions. The fact that E_{pit} was significantly shifted to more noble direction in alkaline brines is in line with the well-established pitting inhibition effect of hydroxyl ions[8]. No explanation can, however, be provided as to the cause of more noble E_{pit} value for Alloy 825 in alkaline salt solution. Finally, no consistent pattern on the effect of Cl⁻ concentration and pH on E_{prot} was observed in this study.

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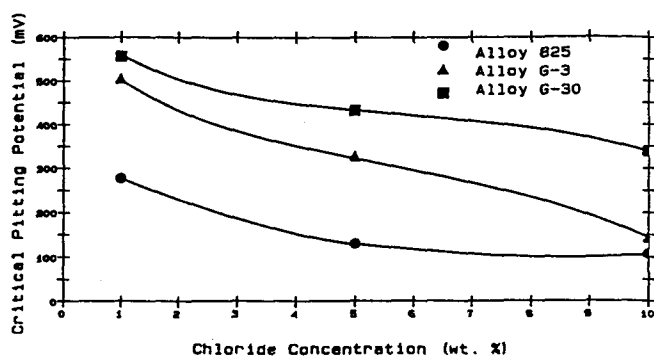
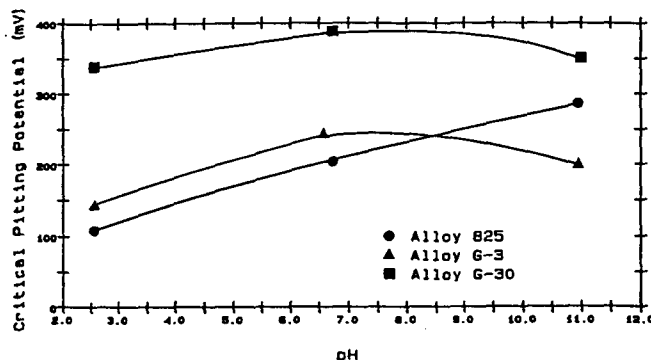Figure 1. Critical Pitting Potential (E_{pit}) vs Chloride Concentration in Acidic Solutions at 90°C

Figure 2. Critical Pitting Potential (E_{pit}) vs pH in Aqueous Solutions Containing 10 wt% NaCl at 90°C

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